Reply to Comment on “Distortions in Octahedrally Coordinated d^0 Transition Metal Oxides: A Continuous Symmetry Measures Approach”

We wish to thank Prof. V. B. Nalbandyan for his Comment on our paper “Distortions in Octahedrally Coordinated d^0 Transition Metal Oxides: A Continuous Symmetry Measures Approach”.

(i) Prof. Nalbandyan states the division of the d^0 cations has been known for decades. We respectfully disagree. The excellent article by Gopalakrishnan and Bhuvanesh[1] does discuss d^0 cations, along with d^0-d^1 systems. In the paper, however, specific strengths of the d^0 distortions are not given, nor are any quantifications made. The excellent article by Brown[2] discusses cation coordination and radii for numerous elements and predicts coordination numbers as well as bond distances. Again, however, specific distortion strengths and magnitudes among d^0 MO_6 octahedra were not discussed. In our paper, we should have referenced another paper by Brown and Kunz.[3] We regret this omission.

(ii) Prof. Nalbandyan states that we omitted Re^{7+} in our compilation. Our paper was written with materials properties in mind, and we felt including Re^{7+}, as well as Sc^{3+} (another d^0 transition metal), would be irrelevant to the reported study. Also, a search of the ICSD database revealed 54 examples of binary and ternary Re^{7+} oxides. Many of these structures are redundant, that is, the same compound, and in most instances the Re^{7+} ion is not in an octahedral environment.

(iii) Prof. Nalbandyan also questions why we did not include Keggin-type ions in our study. Our article focused on solid-state oxide materials—compounds that exhibit one-, two-, or three-dimensional crystal structures. It is true, however, that in some Keggin ions the Mo^{6+} distorts toward a vertex, but these are not extended structures.

(iv) Prof. Nalbandyan questions our methodology for selecting the materials for analysis. As stated clearly in our paper, we used over 75 examples for each d^0 transition metal (Mo^{6+}, V^{5+}, W^{6+}, Ti^{4+}, Nb^{5+}, Ta^{5+}, and Zr^{4+}) octahedra (MO_6). For Hf^{4+} only 27 examples could be found. All of the chosen examples are from materials with reliable crystal structures, as indicated in the ICSD. As is also stated in the article, 762 distinct MO_6 octahedra were examined from 394 independent crystal structures. Thus, some of the materials have more than one unique d^0 MO_6 octahedron. All crystallographically independent MO_6 octahedra were included in our study. In addition, the materials were chosen without regards to symmetry—crystallographic or local site symmetry of the d^0 cation. In examining each MO_6 octahedron, the atomic coordinates of seven atoms were used. That is, the d^0 cation plus the six oxygen ligands. All of the data have been deposited in Supporting Information.

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Kang Min Ok and P. Shiv Halasyamani*

Department of Chemistry and the Center for Material
Chemistry, University of Houston,
Houston, Texas 77204-5003

David Casanova, Miquel Llunell, Pere Alemany, and Santiago Alvarez

Departament de Química Inorgànica, Departament de
Química Física, and Centre de Recerca en Química Teórica,
Universitat de Barcelona, Martí i Franquès 1-11,
08028 Barcelona, Spain

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